CHAPTER V

RESONANT SCATTERING

5.1 INTRODUCTION :-

In the previous chapters, the effect of various factors on the scattering cross section, was observed. Inspite of the best efforts made by various authors to explain the anomalies in the scattering cross section, the larger cross section of some of the polar molecules namely H_2O, H_2S, D_2O could not be accounted satisfactorily. To explain the larger cross section, Turner (1966) made the major break through in the problem. He suggested that, the incident electron might be captured temporarily by the molecule, which means that there is a possibility of the formation of temporary negative ions. It was thought to be, due to the rotational motion of the molecule. This type of phenomena is known as the resonance effect. Temporary negative ions may contribute in the diffusion cross section. The study of life time of the negative ion and the capture cross section is therefore essential. In this chapter an attempt is made to study this phenomena.

Before we discuss resonances in molecules and molecular ions, that is states in which an electron is temporarily retained by a molecular system, we shall make a brief review of the work done. Such a resonance is not a true bound that is stationary state but is a temporary state, capable of decaying by electron emission. In collision processes the formation of a resonance from the target and projetile can be observed. It generally leads to a severe distortion of the projectile wave function. This will be the case provided the life time T of the resonance is long compared with the time the projectile takes to traverse the target.

Resonance in atoms have been reviewed by Burke (1965) and Smith (1966) and resonance in molecule is reviewed by Bardsley and Mandl (1968). In molecules a whole wealth of new features arise owing to the motion of the neclei. In particular there can be an exchange of energy between electronic and neclear motion which shows up in elastic scattering and in inelastic processes such as vibrational and rotational excitation. The comparative long life time of a resonance will lead to severe distortion of the nuclear motion and greatly enhanced inelastic cross sections. Another new feature results from the possibility of the molecular resonance complex dissociating and this process will occur in competition with the reemission of the electron.

The basic physical property of molecule is the large ratio of nuclear to electronic masses. This leads to nuclear velocities being very slow compared with electronic velocities. This is the basis of the Born oppenheimer ~~approximation~~ separation of electronic and nuclear motions. A modification of this approach also leads to a wave equation for the nuclear motion in an electronic resonant state. This equation allows for the decay of resonance in which the nuclei move, and in the case of electron scattering for the formation of the resonanc~~n~~e through electron capture by the target.

5.2 Types of resonance in molecules :-

For a resonance to occur there must be some mechanism for binding the electron temporarily to the target. We can clasify resonances according to the means by which the projectile is trapped.

1. Shape resonances.

The simplest trapping mechanism is a potential barrier. Let us suppose that the incident particle experiences a region of attractive potential surrounded by a region of repulsive potential. If the particle enters the region of attractive potential its escape will be hindered by the potential barrier surrounding it Resonance which are supported by potential barriers will be called shape resonances.

In the simplest shape resonance the electronic motion of the target is effected little by the presence of the incident particle. In this case the dominated terms of the wave equation are the terms containing ground electronic state.

There are other shape resonances in which the wave function is dominated by the terms corresponding to an excited electron target state. In these the incident electron excites a target state whose energy is less than the resonant energy. The extra electron has sufficient energy to escape from the target leaving it in the field of the excited target contains a barrier than its escape will be hindered and the electron will become temporarily bound to the target.

The characteristic of shape resonances is that the wave functions are dominated by the open channel componants. In this the important terms are those corresponding to target states with energies less than the resonant energy.

2. Electron excited Feshbach resonances:-

Feshbach resonances occur when the incident electron looses energy in exciting the target and finds itself with insufficient energy to escape, while the target remains in its excited state. Before the electron can be emitted it must reabsorbed energy from the target.

The simplest situation would be that the incident electron excites only a single electronic target state for which the vibrational levels lie above the resonant energy. In the more general case several electronic states of the target may be important but for a Feshbach resonance it must be closed - channel componants which predominates.

The fact that the open channel componants are small means that the resonance is narrow. Thus Feshbach resonances are nearly always narrow although for large nuclear separations some becomes broad. The wave functions for narrow Feshbach resonances can be approximated by the removal of the open channel componants which turns them in to bound states.

Feshbach resonances in molecules can be divided in to two types, depending on whether the kinetic energy of the incident electron is absorbed in to the electronic or nuclear motion.

3. Nuclear excited Feshbach resonances :-

These are the Feshbach resonances in which the kinetic energy of the incident electron is absrobed solely in to the nuclear motion of the target. The collision does not involve excitation of the electronic motion in the target.

The previous two types of resonance can be discussed within the Born Oppenheimer separation of nuclear and electronic motion. In this third type the resonances are formed by an inter change of energy between these two modes, and thus the existance of the resonance is a consequence of the breakdown of the Born Oppenheimer approximation. Thus inclusion of the nuclear motion is essential to the definition of these resonances. If the nuclei were kept fixed the resonances would become stable against electron emission.

The resonance of this type which have received most attention from both theoreticians and experimenters are the vibrationally excited Rydberg states with high principle quantum numbers.

Nuclear excited Feshbach resonance have been observed in low energy electron molecule scattering and also in the ionization of molecules by electron and photom impact. In this type of resonance in low energy electron molecule scattering, first low energy electron collides with a molecule and is trapped through the vibrational excitation of the molecule. Secondly the excess vibrational energy is lost in a collision with another molecule and the negative ion is stabilized.

(a) Rydberg states of neutral molecules :-

Associated with every electronic state of molecular positive ions is a series of states of the neutral molecule formed by additing to the ion an electron in a hydrogenic orbital with high principle quantum number. The higher members of these Rydberg series have very small electron affinities and the energy of many of their excited vibrational states will be above the energy of the lowest vibrational level of the corresponding ion. Thus these states will leads to many resonances which may be observed in low energy electron ion collisions or in the ionization of neutral molecules just above thresold. The existance of these resonances was used by Beutler and Junger (1936) in the determina--tion of the ionization potential of hydrogen.

Excited rotational levels of Rydberg states may also be unstable against electron emission and so leads to resonances. However these resonances will only be observed in those members of the Rydberg series for which the energy required to detach an electron is less than (or of the same order as) the rotational spacing . For the case of hydrogen this means that the outer most electron must move in an orbit with principle quantum number of the order of 30 or more. It will be very difficult to observe these resonances in ionization experiments because of the very small probability for excitation of these levels. However it has been shown by stabler (1963) that in thermal collisions of electrons with molecular positive ions the cross section for the formation of these resonances should be as high as 10^{-13} or 10^{-14} cm^2 .

Both rotationally excited and vibrationally excited resonant states have been examined as possible intermediate states in dissociative recombination. In thermal electron collision with molecular ions these resonances will be formed and they will have life times varying from 10^{-12} to 10^{-5} second. If the Rydberg state can be stabilized against electron emission then recombination will take place. Stabler found that this stabilization could not be achieved by further collisions or by the emission of radiation but Bardsley (1968) has suggested that predissociation may occur sufficiently rapidly for these states to be significant in the recombination. However for predissociation to occur before electron emission it is necessary that the formation of the resonance should have involved vibrational excitation.

(b) Large molecules :-

The resonances formed by vibrationally excited levels of stable electronic states are of particular interest in large polyatomic molecules. In these energy which is transferred from the incident electron is distributed among the many vibrational modes of the molecule. A considerable time may then elapse before the excess energy is concentrated again in one mode so that it can be given back to the extra electron. Thus these resonances will have extremely long life times; in the order of microseconds.

(c) Polar molecules :-

We have observed in the preceeding chapters that there has been controversy in the cause of the high momentum transfer cross section observed in thermal collision of electrons with polar molecules. The cross sections were claculated using Born approximation by Altshuler (1957) and all the observed cross sections were found to exceed the prediction of the theory. A study of this has been made earlier. Turner (1966) has pointed out that most of the discrepancies could be caused by the induced polarization of the molecules.

Turner suggested that high cross sections for these cases could be attributed to the formation of temporary negative ions. He assumed that the interaction between the electron and the polar molecules could lead to bound state with a very small electron affinity. The excited rotational or vibrational levels of the state could then act as resonances in the electron molecule scattering.

The validity of this proposal clearly depends on the existence of weakly bound states of the electron molecule system. Many authors have examined the spectrum of electrons moving in the field of a dipole. They found that if the dipole moment exceeds critical value of 0.64 a.u. there are an infinite numbers of bound states.

Contrarary to the conclusion of several authors this fact does not mean that nuclear excited resonance can exist for molecule whose dipole moment is small. For molecule the small dipole moment there will not be an infinite number of bound electro-nic states of the negative ion, but the combination of the short range electrostatic interaction and the long range dipole field may be sufficient to support a single bound state (Crawford,1967).

5.3 Negative ions :-

Free electrons are captured to molecules in the gas phase in essentially two different ways, dissociatively and non-dissociatively. When electrons are captured via a dissociative process ($AX + e \rightarrow A + X^-$), collisional stabilization is not required to produce a stable negative ion and the quantity of the importance is the capture cross section σ_c as a function of energy, ϵ. In the case of non-dissociative attachment, electron can attach to molecules temporarily ($AX + e \rightleftarrows AX^*$) or permanently ($AX + e \rightarrow AX^{-*} \longrightarrow AX^-$). If the non-dissociative electron attachment process remains an isolated event the negative ion will auto -

ionize. Stabilization of the excited negative ion can occur through collisions or radiation. Thus in the case of non-dissociative electron attachment the cross section for attachment, the life time for autoionization as well as the stabilization cross section are important.

Electron capture has been studied by both Swarm and Beam methods. The Swarm data are usually compared by plotting the attachment co-efficient α, or the probability of attachment per collision h, Vs E/P or Vs the mean energy of agitation. Most of the early work on electron capture achieved by the Swarm method is complicated because of unknown electron energy distribution. The Beam data on the other hand are usually given as negative ion yields, I (ϵ), in a relative units Vs the electron energy, ϵ . Recent improvement of the Beam method and its combination with the Swarm experiment allowed determination of capture cross section as a function of electron energy.

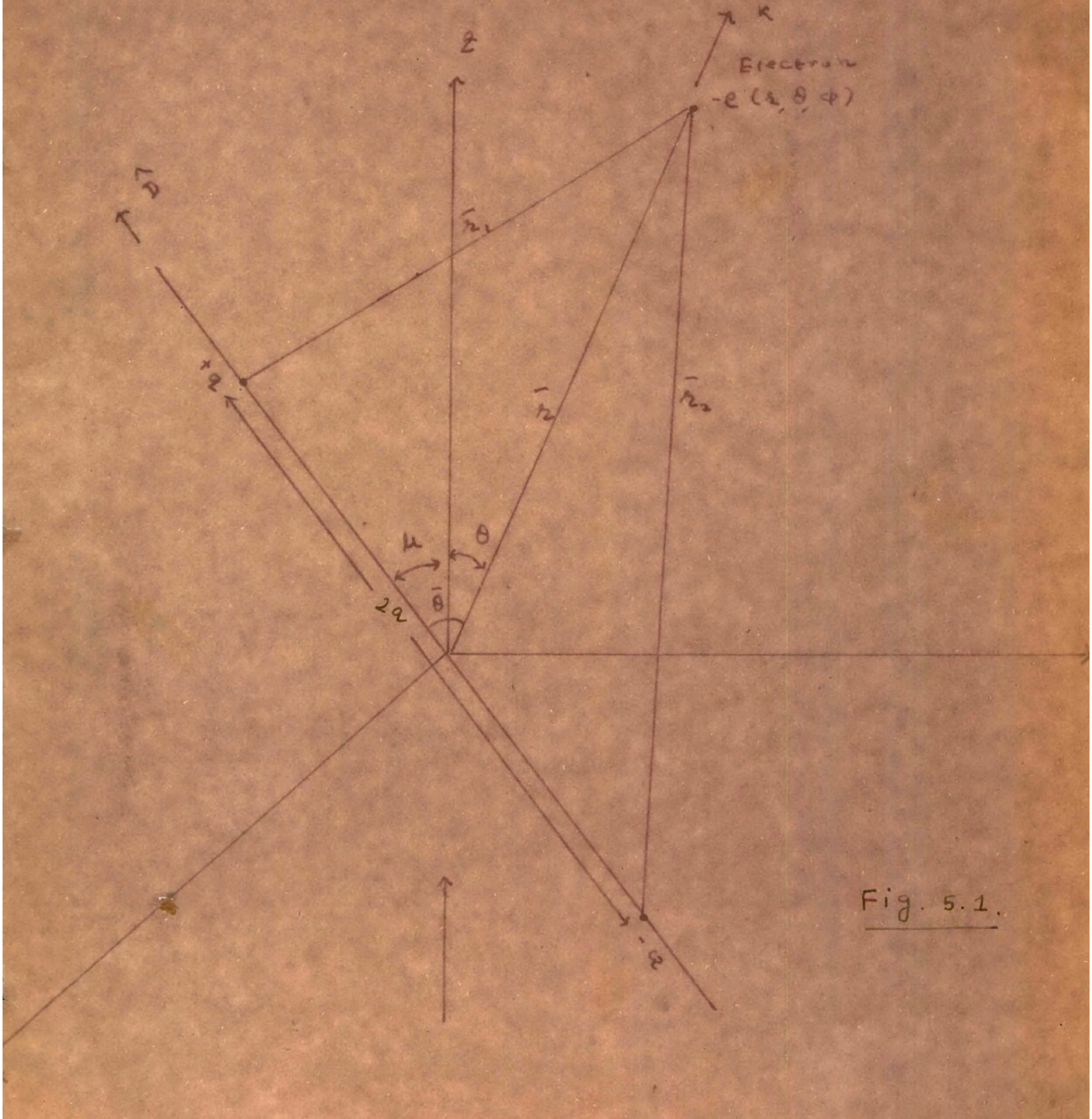
In general, large capture cross section and long life times can be visualized in two manners. (i) weak transitions from the initial state of the neutral molecule directly to a large number of final states of the ion, and (ii) the transition from the neutral molecule to the negative ion is strongly allowed but the excess energy is distributed among the barious internal degrees of freedom. Under assumption (i) large cross sections results because of the large number of final states and long life times are accounted for by the weak coupling between the initial and any of the final states. Under the assumptions (ii) large cross sections result from the large transition probability and the long life times are due to the time required for the system to return to a configuration which will lead to autodetachment.

In case of polar molecules a temporary capture of the electron by the target molecules is suggested by Turner (1966) this gives rise to an enhancement of the total scattering cross section. The possibility of a bound state of an electron in the field of a dipole has been investigated by Wallis et al. (1960), With numerical calculation they have concluded that there is a bound state for a dipole moment larger than 2.14×10^{-18} esu.cm. Turner and Fox (1966) have calculated by variational method the bound state of the electron in the dipole field for dipole moment $0.6\ ea_0$. On the other hand it is shown experimentally that the momentum transfer cross section for electron scattering by some polar molecules, such as H_2O , D_2O , H_2S are appreciably large and do not agree with the results in usual theory. Considering these facts Turner has estimated the effect of the electron capture on the scattering cross section.

According to Turner's model a passing electron can exert a torque on the molecular dipole and might excite the molecule to higher rotational state. The electron might lose enough energy to form a bound state in the field of the dipole. If this state has a finite life time, the decay in to molecule and electron occurs promptly and this process contributes to the scattering cross section.

Turner calculated the capture rate and the life time of the capture state. He showed that the life time is comparable to the period of rotation of molecule. Y.Itikawa (1967) considered the capture process and the decay process in an unified manner. He applied the second order perturbation theory in which the capture state is to be regarded as an intermediate state, has a finite life time.

In the Turner's calculations it was found that the representation for the energy of the electron was approximate. Further though the wave function for the bound state has minimum dipole moment $2.46 ea_0$, which was quite good, it was thought of trying new wave function for this positive energy representation for which also μ_{min} was found equal to Turner's value. It is observed that the effect of these modifications is to increase the life time and to decrease the capture cross section. Again



$\vec{k}$
Electron
$-e\,(r,\theta,\phi)$
z
$\hat{p}$
$\bar{r}_1$
$+q$
$\bar{r}$
$\bar{r}_2$
μ
θ
$\bar{\theta}$
$2a$
$-q$

Fig. 5.1.

the potential used in the calculations was of point dipole model and there seems to be no work on the capture cross section for the finite dipole model. These points are discussed in the present chapter. The calculations are exactly in the same line as that of Turner (1966).

5.4 Resonance for point dipole :-

(i) General formulas.

In fig.1 molecule is represented as a rigid dipole with charges $\pm Q$ separated by a distance 2a. We choose the centre of the dipole as the origin of a set of axis X Y Z which are fixed in space and which we shall call the laboratory system. The polar and azimuthal angles of the dipole relative to X Y Z are denoted by (r, θ , ϕ). We shall also employ polar and azimuthal angles $(\bar{\theta} , \bar{\phi})$ of the electron relative to the dipole. The total Hamiltonian of the system is

$$H = H_M (\bar{\theta}, \bar{\phi}) + H_e (r, \theta, \phi)$$

where $H_M (\bar{\theta}, \bar{\phi}) = - \hbar^2 \textcircled{H}^2/2I$ is the Hamiltonian of a rigid rotator representing the polar molecules with moment of intertia I. $\textcircled{H}$ represents the total angular momentum of the dipole. The units of $\textcircled{H}$ is $\hbar$. $\textcircled{H}$ depends on (θ, ϕ) coordinates. $H_e(r, \theta, \phi)$

is the Hamiltonian of the electron in the field of the dipole.

$$H_e\,(r,\theta,\phi) = -\frac{\hbar^2\nabla^2}{2m} - \frac{Qe}{r_1} + \frac{Qe}{r_2}$$

∇^2 is Laplacian operator in polar coordinates

$$H = \frac{\hbar^2}{2I}\Theta^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{Qe}{r_1} + \frac{Qe}{r_2} \qquad \text{.... } 5.1$$

Total Hamiltonian H, have eigen function ψ. The eigen function was thought to be equal to the product of the eigen function $\psi\,(r,\theta,\phi)$ of H_e and angular momentum eigen function $y_{LM}\,(\theta,\phi)$. The eigen function $(r,\bar{\theta},\bar{\phi})$ was calculated for fixed dipole coordinates. Further it was assumed that these functions are related adiabetically as suggested by Born and Oppenheimer (1927). Further more the Hamiltonian H_M, representing the rotation of the molecule can be considered as a perturbation which couples the motion of the molecule and the electron. This was suggested first by Massey (1938).

Consider an electron swarm moving through a gas consisting of N identical randomly oriented polar molecules per unit volume. If initially an electron is in a positive energy eigen state ψ_i normalized to unit volume and the molecule is in an angular momentum eigen state $y_{L_iM_i}$, then the transition probability for capture of the electron to state ψ_f with simulteneous excitation of the molecule to a rotational state $y_{L_f M_f}$ is given given by $W = \frac{2\pi}{\hbar} \left| T_{f_i} \right|^2 N \; f(E)$

$$= \frac{2\pi}{\hbar} \left| \left\langle \psi_f y_{L_f M_f} \right| \left(- \frac{\hbar^2}{2I} \omega^2 \right) \left| \psi_i y_{L_i M_i} \right\rangle \right|^2 N f(E) \qquad \ldots 5{\cdot}2$$

It is assumed that the electron swarm is characterized by an energy distribution ~~o~~for which $f(E)dE$ represents the probability of finding an electron with energy between E and E + dE. It is understood that the energy E to be used in equation 5·2 is the particular value of the electron kinetic energy for which energy is conserved in the transition $\psi_i \, y_{L_i M_i} \rightarrow \psi_f \, y_{L_f M_f}$. Transitions to a definite final state thus select electrons from the swarm in a narrow energy interval dE, the breadth of which is determined by the life time of the final state.

The capture cross section is defined in terms of the average speed v_o of the eleectron is $\sigma_c = W/V_oN$ =

$$\left(\frac{2\pi}{\hbar \nu_o} \right) \left| T_{f_i} \right|^2 f(E) \quad \ldots\ldots \qquad \ldots\ldots \quad 5{\cdot}3$$

with $\nu_o = \int_0^\infty (2E/m)^{1/2} \, f(E) \, dE \qquad \ldots\ldots \quad 5{\cdot}4$

and $f(E) = \frac{2}{\sqrt{\pi} (KT)^{3/2}} E^{1/2} e^{-E/KT} \qquad \ldots\ldots \quad 5{\cdot}5$

Here K = Boltzman constant.

The quantity σ_c is measured experimentally provided the negative ions formed by capture are stabilized before they have a chance of decay, i.e. provided the life time of the ion is long compared with the time needed for transfer of the excitation energy to another molecule by collision. When the ions are stabilized the expression 5·3 should be multiplied by a pressure factor $p/(p + p')$, where p is the gas pressure and p' is the critical pressure, at which the life time of negative ions is equal to the time needed for transfer of the excitation energy. The estimate below show that stable ions are not formed, hence we make no use of pressure factor.

For the estimation of life time of the negative ion it is necessary to calculate the matrix element " T_{f_i} " for the decay between two states $\psi_f \, y_{L_f M_f}$ and $\psi_i \, y_{L_i M_i}$, the life time T is given by $T = \hbar / 2\pi |T_{f_i}|^2 \, dn/dE$ .... 5·6

where dn/dE represents the density of the final states. The value of dn/dE for free electron and neutral molecule is given by $K^2 / 2\pi^2 \hbar \nu$. $\hbar\nu$ is the magnitude of the momentum of the electron and hence $T = \pi \hbar^4 / m \, (2 E m)^{1/2} \, |T_{f_i}|^2$ ...... 5·7

(ii) Wave functions and evaluation of transition matrix:-

(I) Initial states:-

To calculate the transition probability for electron capture explicitly, we next determine the wave function involved. For the initial and final rotational eigen states of the molecule, $y_{L_i M_i}$ and $y_{L_f M_f}$, we choose the normalized spherical harmonics as defined by Bethe and Salpeter (1957).

For the electronic wave function we assumed that the wavelength of an electron in a swarm at thermal energies is long compared with the extension 2a of the molecular dipole and that in the trapped state the electron is only loosely bound over a volume with dimensions large compared to 2a. We then approximate the interaction of the electron with the molecule by the interaction of the electron with a point dipole. Expanding the potential energy part of H_e in terms of Legendre polynomials involving the orientation $\bar{\theta}$ of the position of the electron with respect to the dipole axis and keeping only the lowest order term, we obtain from equation 5.1

$$H_e \psi_i = \left\{ - (\hbar^2/2m) \nabla^2 - (D e / r^2) \cos \bar{\theta} \right\} \psi_i = E_c \psi_i \qquad \ldots\ldots 5.8$$

where D = 2aQ is the dipole moment of the molecule and E_c is the electron energy in the captured state ($E_c < 0$). In terms of the initial kinetic energy E of the electron and the rotational excitation energy ΔE of the molecule, the conservation of energy requires that ΔE is equal to $E - E_c$.

We regard the initial electron state as consisting of the sum of plane wave e^{iKZ}, with the wave number $K = \left(\frac{2mE}{\hbar}\right)^{1/2}$ incident along the positive Z axis in the laboratory system and an outgoing spherical wave $f(\theta,\phi)\frac{e^{iKr}}{r}$ of relatively small amplitude that represents elastic scattering from the dipole with a fixed orientation (θ,ϕ) in space.

$$\Psi_i(r) = e^{iKZ} + f(\theta,\phi)\frac{e^{iKr}}{r} \qquad \ldots\ldots \qquad \ldots\ldots \qquad 5.9$$

where $$f(\theta,\phi) = -\frac{m}{2\pi\hbar^2}\int e^{iK\bar{n}\cdot\bar{r}'}\, V(r')\,\Psi_i(r')\,dr' \qquad 5.10$$

Turner calculated the amplitude factor considering Born approximation. In chapter IV the effect of variation method to scattering amplitude was made. It was observed that in some of the cases variational approach gave better results than Born approximation. Hence in the present study the variational amplitude factor is used in place of Born amplitude. Using variational method of L.Mower (1955) exactly as it is used in Chapter IV the expression for $f(\theta,\phi)$ can be put up as

$$f(\theta,\phi) = \frac{2\,i\,D'e\,m}{\hbar^2 K}\left[1 + T_0(\theta)\right] \qquad \ldots\ 5.11$$

To write equation 5·11 explicitly in terms of (μ, ν) and (θ, ϕ), we form the scalar product of K with the unit vector D along the dipole axis in the direction from the origin to the charge + Q

$$K \cdot D = K\gamma' = \alpha K_x + \beta K_y + \gamma K_z \qquad \ldots\ldots \qquad 5{\cdot}12$$

Here $K_x\ K_y\ K_z$ are the componants of K in the laboratory system and α, β and γ are the direction cosine of D in this system.

$$\begin{aligned} \alpha &= \sin\mu \cos\nu \\ \beta &= \sin\mu \sin\nu \qquad \ldots\ldots \qquad 5{\cdot}13 \\ \gamma &= \cos\mu \end{aligned}$$

The initial momentum K_o of the electron is directed along the positive Z axis and so,

$$\begin{aligned} K_x &= K_{ox} - K_x = - K \sin\theta \cos\phi \\ K_y &= K_{oy} - K_y = - K \sin\theta \sin\phi \qquad \ldots\ldots \qquad 5{\cdot}14 \\ K_z &= K_{oz} - K_z = K(1 - \cos\theta) \end{aligned}$$

As indicated in fig.I K = 2k sin 1/2 θ and so we write in place of equation 5·11

$$f(\theta, \phi) = \frac{i D e m}{2 \hbar^2 K} - \frac{\alpha \sin\theta \cos\phi - \beta \sin\theta \sin\phi + \gamma(1 - \cos\theta}{\sin^2 \theta/2}$$

$$X \left\{ 1 - \frac{D e m}{2 \hbar^2} - \frac{\alpha \sin\theta \cos\phi - \beta \sin\theta \sin\phi + \gamma(1 - \cos\theta}{\sin \theta/2} \right.$$

5·21

This expression combined with 5.9 gives the initial state electron wave function. Note that the f depends on the coordinates of the dipole in the laboratory system through α, β, γ and equation 5.13

(II) Bound state wave function :-

For the final bound state Turner choosed a function for the electron which is a sum of S and P states referred to angles ($\bar{\theta}, \bar{\phi}$) of the electrons position relative to the dipole axis. He analysed this wave function and found that smallest value of D for which bound state exist is $2.46\ ea_o$. It must be mentioned that the flexibility of his wave function was very great. Later on he analysed the bound state problem by variation method and found that the minimum value of $D = 0.9\ ea_o$. It was thought (Desai et al 1974) whether any other distribution function can be tried, and if so what results are expected from it. Thus an attempt is made to consider

$$\psi_f = \frac{N}{1 + p^2r^2} \left(C_o Y_{oo} + C_1 Y_{1o} \right) \quad \ldots\ldots \quad 5.16$$

where N = usual normalization factor p = parameter = Z/a_o

Normalization is carried out in the usual manner requiring that $|C_o^2| + |C_1^2| = 1.$ This r distribution function is known as Cauchy's distribution function. Using this function the values for C_o and C_1 were found and it came out to be same as Turner's value. Next the calculations are made for the minimum dipole moment on the same line as Turner, accordingly let

$$\langle H \rangle = \langle T \rangle + \langle V \rangle$$

As derived in detail in appendix I the value of $\langle H \rangle$ becomes

$$H = \frac{e^2 a_o p^2}{2} \left[1 + 4 C_1^2 \right] - \frac{4 D e C_o C_1 p^2}{\sqrt{3}}$$

Now considering the value of $p = Z/a_o$, the value of $\langle H \rangle$ turns out to be exactly similar to Turner's value as

$$\langle H \rangle = Z^2 \left[\frac{e^2}{2a_o} (1 + 4 C_1^2) - \frac{4 D e C_o C_1}{\sqrt{3}\, a_o^2} \right]$$

Then following the Turner the minimum value of the dipole moment (D), which can give the bound state can straight forward calculated by setting $\langle H_e \rangle = 0$, solving for D, and then again setting $\frac{\partial D}{\partial C_1} = 0$, gave the value of $C_1 = 1/\sqrt{6}$. The value of $D_{min} \geqslant 2.46 \times 10^{-18}$ esu. These values are naturally same as Turner. Finally we express the angular variables in the trial function 5.16 in terms of the coordinates (μ, ν) and $(\theta\ \phi)$

of the dipole and the electron in the laboratory system with $Y_{00} = 1/(4\pi)^{1/2}$, $C_0 = \sqrt{5/6}$ and $C_1 = 1/\sqrt{6}$, we obtain from the additional theorem for spherical Harmonics

$$\varphi_f = \frac{2}{\sqrt{6}} \left\{ \frac{Z}{a_o} \right\}^{3/2} \frac{1}{\sqrt{\pi}} \frac{1}{1+p^2r^2} \left[\left\{ \frac{5}{4} \right\}^{1/2} + \right.$$

$$\left. \left\{ \frac{4}{3} \right\}^{1/2} \times \left(y^*_{00} Y_{00} + y^*_{10} Y_{10} + y^*_{11} Y_{11} \right) \right. \qquad 5.17$$

The function y depends on (μ, ν) and Y on (ϑ, ϕ).

The exactly similar behaviour of the wave function $\frac{1}{1 + p^2r^2}$, suggests that this function may be used in place of Turner's wave function e^{-Zr/a_o}; harmlessly to the problem. Moreover in the final results it is observed that choice of this particular function gave better results then e^{-Zr/a_o}.

To study the behaviour of resonance with different aspects, the three modifications in Turner's work are applied, namely

(i) In place of Born approximation scattering amplitude, the variational amplitude is used.

(ii) In the final bound state the modified wave function of the form $1/1 + p^2r^2$ is used.

(iii) Above mentioned two modifications are made simultaneously.

Effects of these modifications in transition probability and hence to the life time of temporarily formed negative ion and capture cross section, are discussed in the next section.

5.5 Evaluation of the matrix element for transition probability:-

The matrix element in 5.2 can now be written with the help of equation 5.9 and 5.17 in the form

$$T_{f_i} = - \frac{\hbar^2}{2I} \left\langle \psi_f \, y_{L_f M_f} \right| \textcircled{H}^2 \left| \psi_i \, y_{L_i M_i} \right\rangle =$$

$$- \frac{\hbar^2}{I\sqrt{6}} \left\{ \frac{Z}{a_o} \right\}^{3/2} 1/\sqrt{\pi} \iint \frac{1}{1 + \beta^2 r^2} \quad (5/4 \pi)^{1/2} +$$

$$\left\{ \frac{4\pi}{3} \right\}^{1/2} X \; (y^*_{00} \; Y_{00} + y^*_{10} \; Y_{10} + y^*_{11} \; Y_{11}) \quad y^*_{L_f M_f} \quad X$$

$$\textcircled{H}^2 \left[e^{iKZ} + f(\theta, \phi) \frac{e^{iKr}}{r} \right] y_{L_i M_i} \, d^3r \; d\Omega \qquad \ldots 5.18$$

in which $d\Omega = d(\mathrm{Cos}\,\mu)\, d\nu$ and $f(\theta, \phi)$ is understood to depend on μ and ν through the relationship 5.15 and 5.13. The molecular rotational states $y_{L_f M_f}$ and $y_{L_i M_i}$ are orthogonal and hence equation 5.18 can be written as the sum of three integrals

$$T_{f_i} = - \frac{\hbar^2}{I\sqrt{6}} \left\{ \frac{Z}{a_0} \right\}^{3/2} \frac{1}{\sqrt{\pi}} \left[I_1 + I_2 + I_3 \right] \quad \ldots 5{\cdot}19$$

with

$$I_1 = \left\{ \frac{5}{4\pi} \right\}^{1/2} \iint \frac{1}{1 + p^2 r^2} X^* \; y^*_{L_f M_f} \; X \; \Theta^2 f(\theta, \phi) \; \frac{e^{iKr}}{r} \; y_{L_i M_i} \, d^3r \, d\Omega \quad (5{\cdot}20)$$

$$I_2 = \left\{ \frac{4\pi}{3} \right\}^{1/2} \iint \frac{1}{1 + p^2 r^2} X \left(y^*_{00} Y_{00} + y^*_{10} Y_{10} + y^*_{11} Y_{11} \right) y^*_{L_f M_f} \; X \; \Theta^2 \; e^{iKZ} \; y_{L_i M_i} \, d^3r \, d\Omega \quad (5{\cdot}21)$$

$$I_3 = \left\{ \frac{4\pi}{3} \right\}^{1/2} \iint \frac{1}{1 + p^2 r^2} \left(y^*_{00} Y_{00} + y^*_{10} Y_{10} + y^*_{11} Y_{11} \right) y^*_{L_f M_f} \; X \; \Theta^2 f(\theta, \phi) \; \frac{e^{iKr}}{r} \; y_{L_i M_i} \, d^3r \, d\Omega \quad (5{\cdot}22)$$

The evaluation of these integrals is straight forward but very lengthy. Moreover it was observed that for low energy ranges $I_2 \rightarrow 0$. The three corrections stated in the last section, gave three different form of T_{f_i}.

First of all an attempt is made to calculate transition probability consdering the amplitude correction only.

It is observed that variational amplitude together with wave function for final bound state as e^{-Zr/a_o}, gave T_{f_i} as

$$T_{f_i} = \frac{1\,D\,e\,m}{I\,K\sqrt{6}} \left\{\frac{a_o}{Z}\right\}^{1/2} \Big[2\,(5\pi)^{1/2} \Big(S_{f_i}^{(1)} - \frac{2\,D\,e\,m}{3\,\hbar^2} \Delta S_{f_i}^{(1)} \Big) + (3\pi)^{1/2} \Big(S_{f_i}^{(3)} - \frac{4\,D\,e\,m}{3} \Delta S_{f_i}^{(3)} \Big) \qquad \text{......(5.23)}$$

where $S_{f_i}^{(1)}$, $\Delta S_{f_i}^{(3)}$, $\Delta S_{f_i}^{(1)}$, $\Delta S_{f_i}^{(3)}$ are defined as

$$S_{f_i}^{(1)} = L_f\,(L_f + 1) \Big[\alpha(L_i\,M_i)\,\delta_{L_f,\,L_i+1} + \beta(L_i M_i)\,\delta_{L_f,\,L_i-1} \Big] \delta_{M_f M_i} \qquad (5.24)$$

$$\Delta S_{f_i}^{(1)} = L_f\,(L_f + 1)\;\delta_{L_f L_i},\;\delta_{M_f M_i} \qquad \text{.......}\quad \text{..(5.25)}$$

$$S_{f_i}^{(3)} = \Big\{ L_i\,(L_i - 1) \Big[\gamma(L_f M_f)\,\eta(L_i M_i) + \epsilon(L_f M_f)\,\zeta(L_i M_i) \Big] \times \delta_{L_f+1,\,L_i-1} + (L_i + 1)(L_i + 2) \Big[\gamma(L_i M_i)\,\eta(L_f M_f) + \epsilon(L_i M_i)\,\zeta(L_f M_f) \Big] \delta_{L_f-1,\,L_i+1} \Big\} \delta_{M_f M_i} \qquad (5.26)$$

$$\Delta S_{f_i}^{(3)} = 1/3 \left[L_i (L_i + 1) - 2 \right] \delta_{L_f L_i} \delta_{M_f M_i} -$$

$$1/5 \left[L_i (L_i + 1) - 4 + i \right] \left\{ \alpha (L_i M_i) \delta_{L_f, L_i + 1} + \beta (L_i M_i) \delta_{L_f, L_i - 1} \right\}$$

$$x \ \delta_{M_f M_i} + 2/5 \left\{ L_i (L_i + 1) + (M_i - 2) \right\} \left\{ \gamma (L_i M_i) + \eta (L_i M_i) \right\}$$

$$\Big[\epsilon (L_f M_f) \sigma (L_i M_i) \delta_{L_f + 1, L_i + 2} - \epsilon (L_f M_f) \rho (L_i M_i) \delta_{L_f + 1, L_i} +$$

$$\zeta (L_f M_f) \sigma (L_i M_i) \delta_{L_f - 1, L_i + 2} + \zeta (L_f M_f) \rho (L_i M_i) \delta_{L_f - 1, L_i} \Big]$$

$$\delta_{M_f + 1, M_i} \qquad (5{\cdot}27)$$

where

$$\alpha (L, M) = \beta (L + 1, M) = \left[\frac{(L + M + 1)(L - M + 1)}{(2L + 1)(2L + 3)} \right]^{\frac{1}{2}}$$

$$\gamma (L, M) = \eta (L + 1, -M + 1) = \left[\frac{(L - M + 1)(L - M + 2)}{(2L + 1)(2L + 3)} \right]^{\frac{1}{2}}$$

$$\rho (L, M) = \sigma (L + 1, M) = \left[\frac{(L + M)(L - M + 2)}{(2L + 1)(2L + 3)} \right]^{\frac{1}{2}}$$

$$\epsilon (L, M) = \zeta (L + 1, -M - 1) = \left[\frac{(L + M + 1)(L + M + 2)}{(2L + 1)(2L + 3)} \right]^{\frac{1}{2}} \qquad (5{\cdot}28)$$

Then the attempt was made to see the correction due to wave function of the form $1/\,1 + p^{2}r^{2}$ to point dipole potential, it is observed that in this case the transition probability becomes

$$T_{f_i} = \frac{i\,D\,e\,m}{I\,K\sqrt{6}}\left(a_0/Z\right)^{1/2}\left\{(5\pi)^{1/2} S_{f_i}^{(1)} + \sqrt{\frac{3\pi}{2}}\, S_{f_i}^{(3)}\right\}$$

$$\left[e^{t} E_i(-t) + e^{-t} E_i(t) + \frac{i}{2} e^{-t}\right] \qquad (5{\cdot}29)$$

Here $E_i(t)$ and $E_i(-t)$ are the exponential integrals, $t = K/p$

$p = Z/a_0$ which leads to the value of $t = \left(\frac{2mE}{\hbar}\right)^{1/2} \frac{\hbar^2}{m e^2 Z}$

considering this value of t $E_i(-t)$, $E_i(t)$, e^{t}, e^{-t} were calculated.

Finally simulteneous application of both the modifications were also studied which gave the transition probability of the form

$$T_{f_i} = \frac{i\,D\,e\,m}{I\,K\sqrt{6p\pi}}\left\{(5\pi)^{1/2}\left[S_{f_i}^{(1)} - \frac{2\,D\,e\,m}{3\hbar^2}\cdot\Delta S_{f_i}^{(1)}\right]\right\} +$$

$$\left\{\frac{3\pi}{2}\right\}^{1/2}\left[\left(S_{f_i}^{(3)} - \frac{4\,D\,e\,m}{3\hbar^2}\,\Delta S_{f_i}^{(3)}\right]\right\}\left\{e^{t} E_i(-t) + \right.$$

$$\left. e^{-t} E_i(t) + \frac{i}{2} e^{-t}\right\} \qquad \ldots\ldots\ldots\ldots \quad (5{\cdot}30)$$

Turner's expression for T_{f_i} is

$$T_{f_i} = \frac{i\,D\,e\,m}{I\,K\sqrt{6}}\left(a_0/Z\right)^{1/2}\left\{2\sqrt{5\pi}\, S_{f_i}^{(1)} + \sqrt{3\pi}\, S_{f_i}^{(3)}\right\} \qquad (5{\cdot}31)$$

Considering an experiment at room temperature transition probability for some of the molecules were calculated, for all the three modifications. By using these T_{f_i}, as discussed in section 5.4 the life time for temporary negative ion and capture cross section were calculated. The values of dipole moment and moment of intertia for the molecules under study are tabulated in table 1. Further table 2, 3 and 4 represents the comparision of transition probability, life time, and capture cross section for all the molecules, for $L = 2 \rightarrow L = 3$ states together with Turner's results. It was further observed from the table that all these three modifications gave higher value of life time and lower value of cross section than Turner's value. The dependence of these quantities on $(D/I)^2$ remains as it is.

For the calculations of life time and capture cross section Turner took the value of $D = 2 \times 10^{-18}$ esu and $I = 10^{-40}$ gm.cm^2. These values are roughly comparable with water molecule. He calculated $T = 1.3 \times 10^{-13}$ seconds, $\sigma_c = 2.4 \times 10^{-14}$ He then tried to compare the life time with the rotational period of the state $L = 3$, which is equal to 1.8×10^{-13} seconds. By this observation he concluded that in the swarm experiment electron in swarm can be attached by means of the rotational excitation of the polar molecules. The attachment is possible for the time less than or comparable to the rotational period of the molecule. The ions do not live long enough, however tobecome stabilized and their decay returns electrons to the swarm, By considering the exact value of dipole moment and moment of intertia for water molecules, the life time for negative ions by Turner's formula is found 6.55×10^{-15} seconds. Applying variation method to the scattering amplitude and by using this amplitude factor in place of Born amplitude, the calculations carried out for T gave the value as 8.189×10^{-15} seconds. The wave function correction gave the value of T as 1.2×10^{-14} and simulteneous application of both this modifications gave the value of life time as 1.5×10^{-14}. Modifications does increases the life time, but for water molecule it remains less than the rotational period of the state $L = 3$. Which means that Turner's conclusion is correct for this particular molecule. It was further observed that Turner's conclusion is correct for the molecules having small moment of in~~t~~ertia. For the molecules like CO_2, HCN, CH_3Cl, CH_3CN, $(CH_3)_2O$ having large moment of inertia, the life time was found to higher than the rotation time of the state $L = 3$. For example in the case of CO_2 molecule life time according to Turner's calculations turns out to be 8.07×10^{-10} seconds. While the modification in -

amplitude and wave function for final bound state gave $1{\cdot}36 \times 10^{-9}$ seconds. Hence for the molecules having large moment of inertia can attached the electron for longer time, which favours the existence of long lived negative ions. The increasing life time was found to reduces the capture cross section.

5.6 Resonance for finite dipole :-

In the earlier section discussions were made on the assumption of a point dipole, however it is well known that this presents lot of anomalies. It was found that finite dipole gave the potential resonance in momentum transfer cross section studies. Whether the extension of the finite dipole model does give more information in the capture cross section or not ? With this idea a study is made of this model to the resonance scattering phenomena.

The scattering amplitude for the finite dipole potential is derived in chapter IV. The expression for this is given by

$$f(\theta,\phi) = 3\left(\frac{\mathrm{Sin}\,Ka}{K^3 a^3} - \frac{\mathrm{Cos}\,Ka}{K^2 a^2}\right) \qquad (5{\cdot}32)$$

on expanding SinKa, CosKa in terms of Ka the expression for $f(\theta, \phi)$ for finite dipole is obtained as

$$f(\theta, \phi) = f_B(\theta, \phi) + f_1(\theta, \phi)$$

where $f_1(\theta, \phi) = \dfrac{2 i D e m \gamma' K a^2}{10 \hbar^2}$

here $a = 1/2$ (Dipole length)

Substituting the values of $f_B(\theta, \phi)$, γ' and K we get the value of $f(\theta, \phi)$ as,

$$f(\theta, \phi) = \frac{i D e m}{2 \hbar^2 K} \left\{ - \frac{\alpha \sin\theta \cos\phi - \beta \sin\theta \sin\phi + \gamma(1-\cos\theta)}{\sin^2 \theta/2} \right\}$$

$$+ \frac{2 i D e m K_0 a^2}{10 \hbar^2} \left\{ - \alpha \sin\theta \cos\phi - \beta \sin\theta \sin\phi + \gamma(1-\cos\theta) \right\}$$

Transition probability T_{f_i} turns out to be

$$T_{f_i} = \frac{i D e m}{I K_0 \sqrt{6}} \left(\frac{a_0}{Z} \right)^{\frac{1}{2}} \Big[2 \left\{ (5\pi)^{1/2} + \left(\frac{\pi}{5} \right)^{1/2} K_0^2 a^2 \right\} S_{f_i}^{(1)} +$$

$$\left\{ (3\pi)^{1/2} + 0.4 \, (3\pi)^{1/2} K_0^2 a^2 \right\} S_{f_i}^{(3)} \qquad \ldots . (5.33)$$

To observe the effect of the wave function $1/1+p^2 r^2$ in the final bound state, the calculations were carried out exactly as discussed in the last section, here it was observed that $\langle H \rangle$ turns out to be

$$\cancel{\langle H \rangle = \frac{e^2 a_0 p^2}{2} (1 \pm 4C_1^2)} - \qquad \text{(Contd.)}$$

$$H = \frac{e^2 a_o p^2}{2} \left[(1 + 4 C_1^2) \right] - \frac{4 N^2 e q C_o C_1}{\sqrt{3}}$$

$$\left[\frac{1}{2 p^4 a^2} \log (1 + p^2 a^2) - \frac{1}{2p^2 (1+p^2 a^2)} - \frac{a^2}{2(1 + p^2 a^2)} \right.$$

$$\left. + \frac{a}{2p} (\pi/2 - \tan^{-1} p/a) \right]$$

The detail of this calculations are given in appendix II.

$$N^2 = \text{Normalization constatn} = 2 p^3 / \beta (3/2, 1/2)$$

or $\langle H \rangle = \mu (t + 1 + 8 C_1^2) - \nu C_o C_1$.

where $t = 1$, $\mu = \frac{e^2 a_o p^2}{4}$

$$\nu = \frac{4 N^2 e q}{2 \sqrt{3}} \left[\frac{\log (1 + p^2 a^2)}{p^4 a^2} - \frac{1}{p^2 (1+p^2 a^2)} - \right.$$

$$\left. \frac{a^2}{1+p^2 a^2} + a/p \left(\pi/2 - \tan^{-1} p/a \right) \right]$$

For $\left\langle \frac{\partial H}{\partial C} \right\rangle = 0$

$C_o = \sqrt{1 - C_1^2}$, it was observed that

$$C_1^2 = 1/2 \pm 4 \mu (64 \mu^2 + \nu^2)^{-1/2}$$

The minimum value of the energy in Rydberg was calculated as

$$\langle H \rangle_{min} = 6\lambda \quad -1/2\ (64\,\mu^2 + \nu^2)^{1/2}$$

which gave the minimum value of dipole moment as -

$$D > ea_o \sqrt{15} / 2 = 4.92 \times 10^{-18} \text{esu.cm.}$$

This value is definitely higher than Turner's value $\sqrt{\frac{15}{4}}\, e\, a_o$. This puts a serious restriction on the choice of the dipole moments for the calculation of the capture cross section. In that respect it must be admitted that Turner's wave function is superior. Still however we thought of calculating the values just for the comparision with the same study of point dipole.

Finally the calculations were carried out for T_{f_i} for the modified wave function to finite dipole potential which lead to

$$T_{f_i} = \frac{i\, D\, e\, m}{I\, K \sqrt{6p\pi}} \Big[\ 2 \left\{ (5\pi)^{1/2} + (\pi/5)^{1/2} K_o^2\, a^2 \right\} S_{f_i}^{(1)}$$

$$+ \left\{ (3\pi)^{1/2} + 0.4\ (3\pi)^{1/2}\, K_o^2\, a^2 \right\}\ S_{f_i}^{(3)} \qquad X$$

$$e^t E_i(-t) + e^{-t} E_i(t) + \frac{i\pi}{2} e^{-t} \qquad \ldots\ldots(5.34)$$

The comparision of transition probability capture cross section and life time for both this correction are exhibited in table 5, 6 and 7. The effect of finite dipole calculation was found to decrease the life time and to increase the capture cross section.

The second order time dependent perturbation theory in which a temporary capture state is to be regarded as an intermediate one, was applied by Y.Itikawa (1967). They accounted for momentum transfer cross section. The magnitude of the cross section however was comparable with the direct scattering by the usual calculation. In the Born approximation further correcting the wave function as

$$K_0 \exp \left\{-Z \,(r/a_0)^t\right\} \left[C_0 Y\,(\,00 \mid \bar{\theta}\,\bar{\Phi}\,) + C_1 Y\,(10 \mid \bar{\theta}\,\bar{\Phi}\,)\right]$$

Turner and Fox (1966) showed that this function can be useful for a dipole moment as small as $1{\cdot}65 \times 10^{-18}$ esu.cm. Which also leads to the momentum transfer cross section comparable to the direct scattering by the usual Born approximation calculations.

From the equation 5.34 for transition probability for the finite dipole it is observed that transition probability consists of two terms D/I and D^3/I with other multiplying positive constants. Since D I Z are all the dependent variables exist together it is very difficult to say that a phenomina similar to potential resonance is possible or not. The inter -

pretation becomes more difficult for the modified wave function. Further from the tables 5, 6 and 7 it can be observed that for a finite dipole amplitude life time of temporary negative ions decreases. This means that finite dipole favours the short live negative ion formation to the first approximation.

TABLE I

The dipole moment and the moment of inertia for the molecules studied for resonance scattering.

No.	Molecule	Dipole moment in Debye	*Moment of intertia $X\ 10^{-40}$ gm cm^2	$(D/I)^2\ X\ 10^{44}$
1	H_2O	1.85	1.923	0.9255
2	H_2S	0.93	3.113	0.08925
3	HCN	2.93	18.93	0.02395
4	CO_2	0.18	65.69	$0.7509\ X\ 10^{-5}$
5	NH_3	1.46	4.516	0.1021
6	CH_3Cl	1.88	63.11	$8.876\ X\ 10^{-4}$
7	CH_3CN	3.96	91.22	0.001835
8	$(CH_3)_2O$	1.30	83.47	$2.424\ X\ 10^{-4}$
9	HCl	1.03	2.71	0.1444

* Values of moment of inertia are taken from the " electronic spectra of polyatomic molecules" by Herzberg published by Vannostrand, London (1966).

Resonance for point dipole potential.

T A B L E 2

Comparative statement of square of the transition matrix T_{f_i}

		Square of transition matrix T_{f_i} X 10^{-48}			
No.	Molecule	Turner's	Variational amplitude correction only.	Wave function correction only.	Symulteneous correction of amplitude and wave function both.
1	2	3	4	5	6
1	H_2O	0.8330	0.6664	0.4511	0.3610
2	H_2S	0.08032	0.06425	0.0435	0.03481
3	HCN	0.02156	0.01725	0.01168	0.009349
4	CO_2	$6.757 X 10^{-6}$	$5.466 X 10^{-6}$	$3.66 X 10^{-6}$	$2.929 X 10^{-6}$
5	NH_3	0.09406	0.07524	0.05094	0.04077
6	CH_3Cl	$7.987 X 10^{-4}$	$6.390 X 10^{-4}$	$5.496 X 10^{-4}$	$4.358 X 10^{-4}$
7	CH_3CN	$1.696 X 10^{-3}$	$1.357 X 10^{-3}$	$9.135 X 10^{-4}$	$7.350 X 10^{-4}$
8	$(CH_3)_2O$	$2.74 X 10^{-4}$	$2.193 X 10^{-4}$	$1.485 X 10^{-4}$	$1.188 X 10^{-4}$
9	HCl	[illegible]	[illegible]	0.07839	0.05632

TABLE 3

Comparative statement of life time for temporary negative ions

		Life time " T " X 10^{-13} seconds.			
1	2	3	4	5	6
1	H_2O	0.06551	0.08189	0.1210	0.1511
2	H_2S	0.6794	0.8492	1.254	1.568
3	HCN	2.531	3.163	4.673	5.839
4	CO_2	8074.0	10100.0	14900.0	18630.0
5	NH_3	0.5801	0.7251	1.071	1.339
6	CH_3Cl	68.28	85.39	100.2	125.2
7	CH_3CN	32.18	40.22	59.40	74.23
8	$(CH_3)_2O$	199.1	248.9	367.6	459.4
9	HCl	0.4199	0.5248	0.7752	0.9687

T A B L E 4

Comparision of the capture cross section.

		Capture cross section X 10^{-14} cm^2.			
1	2	3	4	5	6
1	H_2O	0.5554	0.4402	0.3006	0.2276
2	H_2S	0.05356	0.04204	0.2893×10^{-1}	0.02195
3	HCN	0.01437	0.01139	7.73×10^{-3}	5.389×10^{-3}
4	CO_2	4.506×10^{-6}	3.572×10^{-6}	2.439×10^{-6}	1.846×10^{-6}
5	NH_3	0.0613	0.04358	0.03317	0.02511
6	CH_3Cl	5.326×10^{-4}	4.219×10^{-4}	2.332×10^{-4}	2.133×10^{-4}
7	CH_3CN	0.001131	0.3966×10^{-3}	6.12×10^{-4}	4.634×10^{-4}
8	$(CH_3)_2O$	1.455×10^{-4}	1.153×10^{-5}	7.374×10^{-5}	5.961×10^{-5}
9	HCl	0.03666	0.0337	0.0469	0.0355

Resonance for the finite dipole potential.

T A B L E 5

Comparision of T_{f_i}

		T_{f_i} X 10^{-48}		
No.	Molecule	Turner's	Finite dipole amplitude correction.	Symalteneous correction of amplitude and wave function
1	2	3	4	5
1	H_2O	0.3330	0.3392	0.4542
2	H_2S	0.03032	0.03048	0.04356
3	HCN	0.02156	0.02197	0.01190
4	CO_2	$6.757 X 10^{-6}$	$6.757 X 10^{-6}$	$3.657 X 10^{-6}$
5	NH_3	0.09406	0.09448	0.05114
6	CH_3Cl	$7.987 X 10^{-4}$	$8.052 X 10^{-4}$	$4.358 X 10^{-4}$
7	CH_3CN	$1.696 X 10^{-3}$	$1.756 X 10^{-3}$	$9.504 X 10^{-4}$
8	$(CH_3)_2O$	$2.74 X 10^{-4}$	$2.750 X 10^{-4}$	$1.488 X 10^{-4}$
9	HCl	0.1299	0.1302	0.07046

TABLE 6

Comparision of the life time.

		Life time " T " X 10^{-13} seconds.		
1	2	3	4	5
1	H_2O	0.06551	0.06501	0.1200
2	H_2S	0.6794	0.6781	1.253
3	HCN	2.531	2.434	4.590
4	CO_2	8074.0	8074.0	14940.0
5	NH_3	0.5801	0.5776	1.068
6	CH_3Cl	68.28	67.74	125.1
7	CH_3CN	32.13	31.09	57.44
8	$(CH_3)_2O$	199.1	198.5	366.7
9	HCl	0.4199	0.4138	0.7738

TABLE 7

Comparision of capture cross section.

		Capture cross section X 10^{-14} cm^2.		
1	2	3	4	5
1	H_2O	0.5554	0.5597	0.3031
2	H_2S	0.05356	0.05368	0.02905
3	HCN	0.01437	0.01457	0.007366
4	CO_2	4.506×10^{-6}	4.506×10^{-6}	2.496×10^{-6}
5	NH_3	0.06130	0.06158	$0.3333 \times 10^{-}$
6	CH_3Cl	5.326×10^{-4}	5.369×10^{-4}	2.906×10^{-4}
7	CH_3CN	0.001130	0.001171	6.339×10^{-4}
8	$(CH_3)_2O$	1.455×10^{-4}	1.460×10^{-4}	7.893×10^{-5}
9	HCl	0.08666	0.08683	0.04702

APPENDIX I

Normalization of the wave function.

Wave function (5.16) is given in the form

$$\psi = \frac{N}{1 + p^2 r^2} \left\{ C_0 Y_{00} (\bar{\theta}, \bar{\Phi}) + C_1 Y_{10} (\bar{\theta}, \bar{\Phi}) \right\}$$

For normalization we must evaluate

$$\int \psi \psi^* d\tau = I$$

substituting the values we get

$$I = \iiint \frac{N^2}{(1 + p^2 r^2)^2} \left\{ C_0 Y_{00} + C_1 Y_{10} \right\}^2 r^2 \, dr \sin\theta \, d\theta \, d\varphi$$

$$= N^2 \int_0^\infty \frac{r^2 \, dr}{(1+p^2 r^2)^2} \int_0^\pi \int_0^{2\pi} \left\{ C_0^2 Y_{00}^2 + 2 C_0 C_1 Y_{00} Y_{10} + C_1^2 Y_{10}^2 \right\} \sin\theta \, d\theta \, d\Phi$$

for $C_0^2 + C_1^2 = 1$, we have

$$I = N^2 \int_0^\infty \frac{r^2 \, dr}{(1 + p^2 r^2)^2} = \frac{N^2}{2 p^3} \beta (3/2, 1/2)$$

(β= Beta function $\beta(P, r) = \frac{\Gamma P \, \Gamma r}{\Gamma P + r}$)

$$N^2 = \frac{2 p^3}{\beta(3/2, 1/2)}$$

$$N = \left\{ \frac{2\,p^3}{\beta(3/2,1/2)} \right\}^{\frac{1}{2}}$$

Now $\langle H \rangle = \langle T \rangle + \langle V \rangle$

$$\langle T \rangle = \int \psi^{*}\, T\, \psi \;\; d\,T$$

$$= \int \frac{N}{1 + p^2 r^2} \left\{ C_0\, Y_{00}\, (\bar{\theta}\, \bar{\phi}) + C_1\, Y_{10}\, (\bar{\theta}\, \bar{\phi}) \right\}$$

$$X \left\{ - \hbar^2/2m \;\; 1/r^2 \;\; \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{r} \right) - \hbar^2/2m \, \frac{1}{r^2}\, L^2 \right\}$$

$$X \;\; N/1 + p^2 r^2 \left\{ C_0\, Y_{00}\, (\bar{\theta}\, \bar{\phi}) + C_1\, Y_{10}\, (\bar{\theta}\, \bar{\phi}) \right)$$

$$r^2 \; dr \; \sin\theta \;\; d\theta \;\; d\phi$$

where $L^2 = 1/\sin\theta \;\; \frac{\partial}{\partial\theta} \left(\sin\theta\, \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \;\; \frac{\partial^2}{\partial\phi^2}$

we know that $L^2\, Y_{00} = 0$ and $L^2\, Y_{10} = -2\, Y_{10}$

performing elementary integration we get

$$\langle T \rangle = \frac{e^2\, a_0\, p^2}{2} \;\; (1 + 4\, C_1^2)$$

Now $\langle V \rangle = -N^2 \iiint \frac{C_0\, Y_{00} + C_1\, Y_{10}}{(1 + p^2\, r^2)} \;\; \frac{D\; e\; \mathrm{Cos}\,\theta}{r^2}$

$$\frac{C_0\, Y_{00} + C_1\, Y_{10}}{(1 + p^2\, r^2)} \;\; r^2 dr \, \sin\theta \, d\theta \;\; d\phi$$

perofrming integration

$$\langle V \rangle = - 4 D e C_0 C_1 p^2 / \sqrt{3}$$

$$\langle H \rangle = \frac{e^2 a_o p^2}{2} (1 + 4 C_1^2) - \frac{4 D e C_0 C_1 p^2}{\sqrt{3}}$$

putting $p = Z / a_0$

$$\langle H \rangle = Z^2 \left[\frac{e^2}{2 a_o} (1 + 4 C_1^2) - \frac{4 D e C_0 C_1}{\sqrt{3} a_o^2} \right]$$

which gives the final wave function as

$$\varphi_f = 2/\sqrt{6} \; (Z/a_o)^{3/2} \; 1/\sqrt{\pi} \; 1/ 1+ p^2 r^2$$

$$\times \left[\left(\frac{5}{4\pi}\right)^{1/2} + \left(\frac{4\pi}{3}\right)^{1/2} (y^*_{oo} Y_{oo} + y^*_{10} Y_{10} + y^*_{11} Y_{11}) \right]$$

APPENDIX II

Calculation of $\langle H \rangle$ for a finite dipole.

Finite dipole potential can be expressed as

$$V = -2eq \sum_{K=\text{odd}} \frac{r_<^K}{r_>^{K+1}} P_K(\cos\theta)$$

Now in $\langle H \rangle = \langle T \rangle + \langle V \rangle$, as calculated above

$$\langle T \rangle = \frac{e^2 a_0 p^2}{2} (1 + 4 C_1^2)$$

considering $C_0^2 + C_1^2 = 1$, and in the finite dipole potential expression $K = 1$ we get

$$\langle V \rangle = -\frac{4 N^2 e q C_0 C_1}{\sqrt{3}} \left[\int_0^a \frac{1}{(1 + p^2 r^2)^2} \frac{r^3}{a^2} dr + \int_a^\infty \frac{1}{(1 + p^2 r^2)^2} a \, dr \right]$$

on performing elementary integration we get

$$\langle V \rangle = \frac{-4 N^2 e q C_0 C_1}{\sqrt{3}} \left[\frac{1}{2 p^4 a^2} \log (1 + p^2 a^2) \right.$$

$$\frac{1}{2p^2 (1 + p^2 a^2)} - \frac{a^2}{2(1 + p^2 a^2} +$$

$$\left. a/2p \, (\pi/2 - \tan^{-1} p/a) \right]$$

$$\langle H \rangle = \mu (t + 1 + 8 C_1^2) - \nu C_0 C_1$$

where $t = 1$; $\mu = \dfrac{e^2 a_o p^2}{4}$ and

$$\nu = \frac{4 N^2 e q}{2 \sqrt{3}} \left[\frac{\log (1 + p^2)}{p^4 a^2} - 1/p^2 + a/p \, (\pi/2 - \tan^{-1} p/a) \right]$$

For $\left\langle \dfrac{\partial H}{\partial C} \right\rangle = 0$, $C_0 = \sqrt{1 - C_1^2}$

$$C_1^2 = 1/2 \pm 4 \mu (64 \mu^2 + \nu^2)^{-1/2}$$

For the minimum value of $\langle H \rangle$ we get

$\langle H \rangle_{min} = 6 \mu - 1/2 \, (64 \mu^2 + \nu^2)^{1/2}$, which gives

$$\nu > 2 \mu \sqrt{20}$$

Further substituting ν, μ we get

$$D > \frac{\sqrt{15}}{2} e \, a_o = 4.92 \times 10^{-18} \text{ esu.cm.}$$